SPECTROSCOPIC STUDIES OF PREMIXED LAMINAR FLAMES

S. S. PENNER*

Advisory Group for Aeronautical Research and Development,
NATO, Palais de Chaillot, Paris 16, France

A critical review is presented of the results obtained by spectroscopic observations on flames. The objective of the survey is to examine the status, promise, and deficiencies of combustion spectroscopy in its relation to (a) elucidation of the mechanism of combustion and (b) the solution of technical combustion problems. Since important spectroscopic studies have been carried out on low-pressure flames, a discussion of the probable effects of pressure on laminar flame propagation is also included

DURING recent years a number of articles describing experimental and theoretical studies on combustion spectroscopy has been published. The interpretation of experimental data is usually not clear-cut, as is evident from the fact that lively discussions have been put forward concerning, for example, the significance of 'anomalous' rotational temperatures of OH, the mechanism of carbon formation, the nature of the chemical compound responsible for the hydrocarbon flame bands *etc.* Nevertheless, the time appears appropriate for a critical review of the achievements and promise of combustion spectroscopy, particularly of its relation to (*a*) elucidation of combustion mechanism and (*b*) solution of technical combustion problems. In this review we shall attempt to establish basic principles involved in the quantitative interpretation of flame spectra without, however, becoming involved in detailed problems of spectroscopic analysis.

Since there are no *a priori* reasons for expecting anything like thermodynamic equilibrium in regions of active combustion, we shall begin this survey with a discussion of the meaning of 'temperature' under non-equilibrium conditions. The emission and absorption spectrum of the flame gases can be utilized for a description of the relative populations of chemical species in different energy levels. In customary terminology, we associate with these relative population distributions the rotational, vibrational and electronic temperatures of the molecules.† The precise definition of these quantities is given in Section I. It is also possible, in principle, to utilize spectroscopic studies of Doppler-broadened spectral lines for the determination of translational temperatures of individual molecular species.

* On leave from the Guggenheim Jet Propulsion Center, California Institute of Technology, Pasadena, California. Preliminary work was done at C.I.T. with support from the O.N.R. under Contract Nonr—220(03), NR 015–210.

† Hereafter we shall refer to the rotational, vibrational and electronic temperatures collectively as population temperatures.

Spectroscopic studies of low-pressure combustion flames permit a more detailed exploration of regions of active combustion than ordinary flames because the thickness of the reaction zone is increased as the pressure is reduced. However, the possibility must not be overlooked that the nature of the flame reactions may be altered through a reduction of the pressure. These problems can be investigated, in some detail, by utilizing similarity arguments, and the basic equations describing one-dimensional, laminar flame propagation, as described in Section II.

Experimental results obtained by combustion spectroscopists can be classified broadly as (*a*) information concerning positions of line centers and identification of the chemical species responsible for a given set of pectral lines, and (*b*) quantitative information concerning relative or absolute intensities of spectral lines, from which population temperatures and concentration estimates may be deduced. The identification of chemical species responsible for emission or absorption spectra in the visible and ultraviolet regions of the spectrum is clear-cut for atomic and diatomic constituents but becomes quite complex for polyatomic compounds (*cf* Section III). The determination of population temperatures and concentrations involves formidable experimental and computational difficulties, as is evident, for example, from a review of the work done on the rotational temperatures of OH (*cf* Section IV).

On the basis of the experimental data reviewed in Sections III and IV, some conclusions appear to be justified concerning the relation of combustion spectroscopy to combustion mechanism and to the solution of technical combustion problems (*cf* Section V).

I. METHODS FOR ESTIMATING TEMPERATURES AND CONCENTRATIONS IN REGIONS OF ACTIVE COMBUSTION*

A. Population temperatures—If we were confronted with the problem of defining the meaning of 'temperature,' in the conventional sense, in regions of active combustion, we would be at a loss to do so only if we were unable to specify precisely the desired experimental conditions for measurement. Thus, it is a simple matter to define and evaluate temperatures determined by relative populations of molecules in the various internal degrees of freedom. Depending upon the degree of freedom involved, we designate the results as rotational, vibrational or electronic temperatures. At thermodynamic equilibrium these temperatures are equal to each other and are also equal to the translational temperature (determined, ideally, by a thermocouple measurement), which is defined in terms of the mean kinetic energy of the molecules. In regions of active combustion we do not, in general, expect equipartition of energy, which is established only as the result of molecular collisions following chemical reaction. The absence of equilibrium seems all the more plausible if we remember that the only transport coefficient which cannot be calculated accurately from the kinetic theory of gases is

* For a review of optical methods for measuring flame temperatures, see "Optical Methods for the Determination of Flame Temperatures" by S. S. PENNER, *Amer. J. Phys.* Vol. 17, pp. 422–429, and pp. 491–500, 1949, or "Survey of Optical Methods for the Determination of Temperatures in Rocket Engines" by P. J. DYNE and S. S. PENNER, *J. Amer. Rocket Soc.* Vol. 23, pp. 165–169, 1953. The present discussion will be restricted to a survey of the more elaborate techniques, used by spectroscopists, not to estimate the average state of combustion, but rather to obtain specific information concerning individual degrees of freedom of separate molecular or atomic species.

the thermal conductivity. Theoretical calculation of the thermal conductivity involves the assumption of establishment of equipartition of energy among all the degrees of freedom of the colliding molecules (Eucken approximation), an assumption which is apparently not justified[1].

For simplicity we consider molecules the internal energy (ε_{int}) of which may be represented as the sum of electronic ($\varepsilon_i = \varepsilon_{el}$), vibrational ($\varepsilon_v = \varepsilon_{vib}$), and rotational ($\varepsilon_j = \varepsilon_{rot}$) energies. For non-equilibrium distributions of internal energy we consider the system to be an 'inhibited idealized system'[2, 3] for which

$$\frac{N_{i,v,j}}{N} = \left[\frac{g_j \exp(-\varepsilon_j/kT_{rot})}{\sum_j g_j \exp(-\varepsilon_j/kT_{rot})}\right]\left[\frac{g_v \exp(-\varepsilon_v/kT_{vib})}{\sum_v g_v \exp(-\varepsilon_v/kT_{vib})}\right]\left[\frac{g_i \exp(-\varepsilon_i/kT_{el})}{\sum_i g_i \exp(-\varepsilon_i/kT_{el})}\right] \quad \ldots . \quad (1)$$

where $N_{i,v,j}$ is the total number of molecules per unit volume in the electronic state which is characterized by the index i, in the vibrational energy state which is characterized by the index v, and in the rotational energy state which is characterized by the index j; N = total number of molecules per unit volume; $g_{rot} = g_j$, $g_{vib} = g_v$, and $g_{el} = g_i$ represent, respectively, the statistical weights of the energy states $\varepsilon_{rot} = \varepsilon_j$, $\varepsilon_{vib} = \varepsilon_v$, and $\varepsilon_{el} = \varepsilon_i$; the rotational, vibrational and electronic temperatures are identified by the subscripts *rot*, *vib* and *el*, respectively. For statistical equilibrium among the population of molecules in the internal energy states: $T_{rot} = T_{vib} = T_{el} = T_{int}$ where T_{int} may or may not be equal to the mean translational temperature T of the molecules composing the gas mixture.

The integrated intensity of radiation emitted at the frequency $\nu_{i,v,j \to i',v',j'}$, arising from the change in electronic quantum number of $i \to i'$, in vibrational quantum number of $v \to v'$, and in rotational quantum number $j \to j'$, is well known to be

$$I_{i,v,j \to i',v',j'} = K N_{i,v,j} (\nu_{i,v,j \to i',v',j'})^4 A_{i \to i'} A_{v \to v'} A_{j \to j'} \quad \ldots . \quad (2)$$

where K is a known constant which is independent of the energy of the initial state, $A_{i \to i'}$ equals the transition probability for a change in electronic quantum number from i to i', $A_{v \to v'}$ is the transition probability for a change in vibrational quantum number from v *to* v', and $A_{j \to j'}$ represents the transition probability for a change in rotational quantum number from j to j'. In absorption for the transition $i^\circ \to i''$, $v^\circ \to v''$, $j^\circ \to j''$ Eq. (2) must be replaced by the relation

$$I_{i^\circ,v^\circ,j^\circ \to i'',v'',j''} = K' N_{i^\circ,v^\circ,j^\circ} (\nu_{i^\circ,v^\circ,j^\circ \to i'',v'',j''}) \times A_{i^\circ \to i''} A_{v^\circ \to v''} A_{j^\circ \to j''} \quad \ldots . \quad (3)$$

In general, $\varepsilon_{i',v',j'} < \varepsilon_{i,v,j}$ and $\varepsilon_{i'',v'',j''} > \varepsilon_{i^\circ,v^\circ,j^\circ}$.

Denoting the denominator in Eq. (1) by the symbol Q_{int}, where Q_{int} is obviously a function of the rotational, vibrational and electronic temperatures of the initial state (*i.e.* of the higher energy state in emission and

of the lower energy state in absorption) but is independent of the particular values of the initial energy states used for measurement, then it is apparent that Eqs. (2) and (3) become, respectively,

$$-k\ln \frac{I_{i,v,j\to i',v',j'}}{(\nu_{i,v,j\to i',v',j'})^4\,(g_iA_{i\to i'})\,(g_vA_{v\to v'})\,(g_jA_{j\to j'})} = (\varepsilon_j/kT_{rot}{}^u) + (\varepsilon_v/kT_{vib}{}^u) + (\varepsilon_i/kT_{el}{}^u) + \text{constant} \quad \ldots . \quad (4)$$

and

$$-k\ln \frac{I_{i^\circ,v^\circ,j^\circ\to i'',v'',j''}}{(\nu_{i^\circ,v^\circ,j^\circ\to i'',v'',j''})\,(g_i{}^\circ A_{i^\circ\to i''})\,(g_v{}^\circ A_{v^\circ\to v''})\,(g_j{}^\circ A_{j^\circ\to j''})} = (\varepsilon_j{}^\circ/kT_{rot}{}^l) + (\varepsilon_v{}^\circ/kT_{vib}{}^l) + (\varepsilon_i{}^\circ/kT_{el}{}^l) + \text{constant} \quad \ldots . \quad (5)$$

Here the superscripts u and l have been used in the population temperatures in order to emphasize the fact that the temperatures for the upper (u) or lower (l) energy states are involved.

Rotational temperatures in emission are generally determined from visible and ultraviolet spectra for fixed electronic and vibrational transitions, *i.e.*, fixed values of i, v, and i', v'. Under these conditions $g_iA_{i\to i}$ and $g_vA_{v\to v'}$ are evidently independent of ε_j and Eq. (4) becomes

$$\partial \ln [I_{i,v,j\to i',v',j'}/(\nu_{i,v,j\to i',v',j'})^4\,(g_jA_{j\to j'})]/\partial\varepsilon_j = -1/kT_{rot}{}^u \quad \ldots . \quad (6)$$

Similarly, we obtain from Eq. (5) the result

$$\partial \ln [I_{i^\circ,v^\circ,j^\circ\to i'',v'',j''}/(\nu_{i^\circ,v^\circ,j^\circ\to i'',v'',j''})\,(g_j{}^\circ A_{j^\circ\to j''})]/\partial\varepsilon_j{}^\circ = -1/kT_{rot} \quad \ldots . \quad (7)$$

Explicit relations for vibrational and electronic temperatures can be obtained, respectively, by utilizing Eq. (4) for fixed values of j, j', i, i' or of j, j', v, v', and Eq. (5) for fixed values of j°, j'', i°, i'' or of j°, j'', v°, v''. There are other obvious procedures for utilizing Eqs. (1), (4) and (5) for the determination of population temperatures.

B. Flame temperature measurements from Doppler broadening—Optical methods for the determination of the translational temperature of individual molecular species depend on the fact that at low pressures and elevated temperatures the principal contribution to the finite width of spectral lines results from Doppler broadening, at least in the ultraviolet and short visible regions of the spectrum*. In order to utilize the Doppler effect, it is necessary to perform measurements with instruments of exceedingly high resolving power, such as a Fabry-Perot interferometer or a Lummer-Gehrcke plate†. The Fabry-Perot interferometer has been used for the determination of the translational temperature of CH in low-pressure combustion flames[6].

If the frequency of absorbed or emitted light for the molecules at rest is ν_o, then the actual frequency of light absorbed or emitted by molecules moving with a velocity v_x in the direction of the line of sight is, according to Doppler's principle,

$$\nu = \nu_o\,[1 - (v_x/c)] \quad \ldots . \quad (8)$$

* For a discussion of the shape of spectral lines see, for example, the articles quoted in reference 4.
† For a description of spectroscopic instruments reference should be made, for example, to JENKINS and WHITE[5].

where c represents the velocity of light. However, according to the equilibrium kinetic theory of gases the fractional number of molecules moving with linear velocities between v_x and $v_x + dv_x$ is

$$dn/n = (m'/2\pi kT)^{\frac{1}{2}} [\exp(-m'v_x^2/2kT)]\, dv_x = -(m'c^2/2\pi kT)^{\frac{1}{2}} \times \left[\exp\left\{-m'c^2(\nu - \nu_o)^2/2kT\nu_o^2\right\}\right] d\nu \quad \ldots . \quad (9)$$

where n represents the total number of molecules per unit volume, m' equals the mass per molecule, k is the Boltzmann constant and T equals the translational temperature of the molecule under observation. The spectral absorption coefficient $P(\nu)$ is given by the well known absorption law

$$P(\nu) = \text{constant}\ (-dn/n)\ (1/d\nu) \quad \ldots . \quad (10)$$

since the fractional number of molecules in the indicated velocity range is directly proportional to the fractional absorption of light in the frequency interval between ν and $\nu + d\nu$. Combining Eqs. (9) and (10) leads to the result

$$P(\nu) = I(m'c^2/2\pi kT\nu_o^2)^{\frac{1}{2}} \left[\exp\left\{-m'c^2(\nu - \nu_o)^2/2kT\nu_o^2\right\}\right] \quad \ldots . \quad (11)$$

where $I = \int_0^\infty P(\nu)d\nu$ is the integrated absorption of the spectral line whose center lies at ν_o. The quantity I is a constant for a given number of molecules. It is evident from reference to Eq. (11) that Doppler-broadened lines display a Gaussian distribution for the spectral absorption coefficient. The Doppler half-width is defined by the relation

$$P(\nu_o \pm \Delta\nu_D) = \tfrac{1}{2}P(\nu_o)$$

whence
$$\Delta\nu_D = (\ln 2)^{\frac{1}{2}} (2kT/m'c^2)^{\frac{1}{2}} \nu_o \quad \ldots . \quad (12)$$

or
$$\Delta\lambda_D = (\ln 2)^{\frac{1}{2}} (2kT/m'c^2)^{\frac{1}{2}} \lambda_o \quad \ldots . \quad (13)$$

where $\Delta\nu_D$ and $\Delta\lambda_D$ denote, respectively, the Doppler half-widths in frequency and in wavelength units. Thus the translational temperature can be measured either by determining the spectral half-width of Doppler-broadened lines or, preferably, by fitting the observed intensities to the Gaussian function described by Eq. (11).

It is evident from the preceding discussion that it is possible to measure, by the use of spectroscopic methods, the individual translational temperatures of chemical species which either emit or absorb light under conditions where Doppler broadening obtains. The method is probably applicable for low-pressure flames at short wavelengths where spectral line broadening effects associated with molecular collisions are readily shown to be relatively unimportant[4].

It is possible to generalize the method for determining translational temperatures from spectral line-shape for spectral lines displaying the combined effects of Doppler and collision broadening. This extension involves the use of the 'curves of growth' and requires detailed studies of spectral line contour near the line center and in the wings of the lines*.

* For a discussion of the ' curves of growth ' see, for example, the articles quoted in reference 7.

C. Temperature estimates with the line reversal method—Probably the most widely used method for measuring flame temperatures is the line reversal method. This method falls properly within the scope of the present review because it is, in principle, a method for estimating one of the population temperatures. In combustion spectroscopy it has been employed to estimate electronic temperatures[8] although some of its earliest uses involved the determination of rotational and vibrational temperatures[9], [10].

In a line reversal experiment a continuous or discrete light source is viewed through a flame. At the point of reversal the spectral brightness of the source is identical with that of the flame, *i.e.*, the source cannot be differentiated from the flame when it is viewed through the flame. Under these conditions it is readily shown that the temperature for the degree of freedom responsible for the absorbed radiation is equal to the (known) brightness temperature of the source. Since the reversal method usually involves transitions to and from the ground state, it provides information on the population temperature referred to the ground state. If the population of upper electronic states does not follow a Maxwellian distribution, this fact can be exemplified by using the procedure described by GAYDON and WOLFHARD[8].

For any given transition let T_{rev} represent the reversal temperature, and hence the population temperature of the degree of freedom on which measurements are performed. In general, the apparent values of T_{rev} will be functions of the energy level ε of the upper state involved in a given transition. Thus the population of molecules in the quantum level of energy ε, $\mathcal{N}(\varepsilon)$, may be represented formally by the relation

$$\mathcal{N}(\varepsilon) = \mathcal{N}_0 \exp(-\varepsilon/kT_{rev}) \quad \ldots . \quad (14)$$

where $\mathcal{N}_0$ represents the total number of emitters. For T_{rev} it might be appropriate to write $T_{rev}(\varepsilon)$ in order to emphasize the fact that, for a non-equilibrium system, the apparent reversal temperature is generally a function of ε. From Eq. (14) it follows that

$$\partial \ln [\exp(-\varepsilon/kT_{rev})] / \partial \varepsilon = -1/kT_{rev} \quad \ldots . \quad (14a)$$

By using a relation of the form of Eq. (14*a*), Gaydon and Wolfhard have apparently demonstrated anomalies in electronic energy distribution of various atoms (Fe, Pb, Th) in acetylene–air flames[8].

D. Concentration estimates in regions of active combustion—From the point of view of combustion kinetics it is of evident importance to obtain not only population temperatures but also absolute estimates of concentrations. These calculations require knowledge of absolute values of transition probabilities, which are available for the electronic spectra of many atoms[11] and for some diatomic molecules[12-14], as well as for infra-red vibration-rotation bands of a large number of diatomic, triatomic, and polyatomic molecules[15-19]. The analytical labor required in order to obtain concentration estimates is considerable. Details are outside the scope of the present review. A description of two-path experiments designed to obtain temperature and concentration estimates in flames has been published recently[20]. The results of quantitative studies of the influence of absolute

values of concentrations on observable relative intensities for spectral lines of OH have been summarized in a series of graphs[21].

II. ONE-DIMENSIONAL LAMINAR FLAME PROPAGATION AT REDUCED PRESSURES

Some conclusions regarding the effect of pressure on laminar flame propagation can be drawn without obtaining an explicit solution either to an accurate or to an approximate set of flame equations*.

For one-dimensional steady flow the continuity equation for species K becomes, using the formulation of HIRSCHFELDER and CURTISS[22],

$$\mathrm{d}\left[c_K\,(v + V_K)\right]/\mathrm{d}x = \gamma_K$$

or

$$(m/M_K)\,(\mathrm{d}\varepsilon_K/\mathrm{d}x) = \gamma_K = p^\alpha\,\gamma'_K \qquad \ldots\ (15)$$

where c_K denotes the concentration of species K, v is the mass-weighted average flow velocity of the gas mixture, V_K is the diffusion velocity of species K, x is linear distance, γ_K represents the net rate of production of species K in moles per unit volume per unit time, m is the mass flow rate, ε_K equals the fraction of the total mass flow rate carried by species K, M_K is the molecular weight of species K, γ'_K represents the net rate of production of species K in moles per unit volume per unit time at unit pressure, and α represents an order of the reaction. We may interpret the substitution $\gamma_K = p^\alpha\gamma'_K$ as involving either the assumption that all of the various chemical processes which form or remove species K are of the same order α, or else that the rate-controlling step determining the time rate of change of species K is of order α. Without this approximation the analysis cannot be carried out in a simple way. It is well known that for a given chemical system the adiabatic flame temperature T_f and the equilibrium weight fractions γ_K are relatively insensitive to variations in pressure. Hence it is not unreasonable *to assume that a change in pressure does not alter the character of the flame reactions, as a first approximation.* In this case the group $\mathrm{d}\varepsilon_K/M_K\ \gamma'_K$ will be approximately independent of pressure. Thus we obtain from Eq. (15) the result

$$\int_{\Delta x} \mathrm{d}\varepsilon_K/M_K\,\gamma'_K = p^\alpha.\quad \Delta x/m = \text{constant (for fixed initial composition and initial temperature)} \qquad \ldots\ (16)$$

where Δx denotes the thickness of the reaction zone. The constant in Eq. (16) is obtained conveniently by choosing conditions at atmospheric pressure (which will be identified by the subscript 1) as reference state. Thus Eq. (16) leads to the relation

$$m/\Delta x = (m_1/\Delta x_1)\,p^\alpha \qquad \ldots\ (17)$$

The general diffusion equation can be written[22, 23] in the form

$$\mathrm{d}X_K/\mathrm{d}x = \left[m/\sum_K c_K\right] \sum_{j,K} (1/D_{K,j}) \left[(X_j\varepsilon_K/M_K) - (X_K\varepsilon_j/M_j)\right] \qquad \ldots\ (18)$$

where X_K is the mole fraction of species K and the $D_{K,j}$ are binary diffusion coefficients for interdiffusion of species K and j. The quantities

* The results of the present analysis are well known and have been given by several authors. Dr THEODORE VON KÁRMÁN has pointed out that the argument is essentially a dimensional analysis.

$X_K, X_j\varepsilon_K/M_K$, and $X_K\varepsilon_j/M_j$ are roughly independent of pressure; $\sum_K c_K$ is proportional to the first power of the pressure whereas $D_{K,j}$ varies roughly inversely as the pressure. Hence we obtain from Eq. (18) the result

$$m\Delta x = \int_{\Delta x} \mathrm{d}X_K \left[\sum_{j,K} (1/D_{K,j}) \left\{ (X_j \varepsilon_K/M_K) - (X_K \varepsilon_j/M_j) \right\} \right]^{-1} \sum_K c_K$$

$$= \text{constant (for fixed initial composition and initial temperature)} \quad \ldots . \quad (19)$$

whence

$$m\Delta x = m_1 \Delta x_1 \quad \ldots . \quad (20)$$

The condition for conservation of energy can be written[22, 23] as

$$m(\mathrm{d}/\mathrm{d}x) \left[\sum_K (\varepsilon_K H_K/M_K) - (\lambda/m)\,(\mathrm{d}T/\mathrm{d}x) \right] = (m/\rho)\,(\mathrm{d}p/\mathrm{d}x) \quad \ldots . \quad (21)$$

where H_K denotes the molar enthalpy of species K, λ is the thermal conductivity, T the temperature, ρ the density of the gas mixture, and p the hydrostatic pressure. Here H_K and λ are practically independent of pressure and $(m/\rho)\,(\mathrm{d}p/\mathrm{d}x)$ is practically zero. Hence Eq. (21) again leads to the result given in Eq. (20).

Combining Eqs. (17) and (20) leads to the relations

$$m = m_1 p^{\alpha/2} \quad \ldots . \quad (22)$$

$$\Delta x = (\Delta x)_1 p^{-\alpha/2} \quad \ldots . \quad (23)$$

and

$$v = v_1 p^{(\alpha/2)-1} \quad \ldots . \quad (24)$$

From Eq. (23) it is evident that for all chemical reactions the thickness of the flame front increases as the pressure is diminished. In particular, for $\alpha = 2$, the thickness of the flame front varies inversely as the pressure, a result which is in accord with available experimental data. For $\alpha = 2$ it is apparent that the linear burning velocity v is independent of pressure.

Since most elementary reaction processes proceed as the result of binary collisions one might expect the effective overall or global reaction to have a value of α close to two. Hence the conclusion is reached that v should depend either not at all or else only weakly on the pressure. The last statement is in accord with experimental studies on low-pressure flames[24] and is not contradicted by the studies of TANFORD and PEASE[25], who postulate a definite mechanism for the rate-controlling reaction step.

It is of interest to note that for $\alpha = 2$ the number of collisions in the reaction zone n_c becomes independent of the pressure, thereby amplifying the initial postulate that the character of the flame reactions is not changed by a change of pressure. Thus it is known from the kinetic theory of gases that the mean free path $\bar{l}$ is nearly inversely proportional to the pressure, whence

$$n_c = \Delta x/\bar{l} = (\Delta x_1/\bar{l}_1) p^{1-(\alpha/2)} \quad \ldots . \quad (25)$$

Emission of radiation is a first-order process. Hence, even if on the average the same chemical species are formed at reduced pressures as at elevated pressures, deactivation of excited molecules by emission of radiation

must be enhanced relative to deactivation by collision, as the pressure is lowered. As a consequence of this effect, it is expected that the total radiation intensities in emission increase for a given amount of combustible material. The absolute value of the increase in intensity is evidently a function of the radiative life of the excited species and of the pressure range which is being considered.

Additional insight into the probable effect of pressure on laminar flame propagation is obtained by the following considerations. It is known from chemical kinetics[26] that the chain-starting reactions are usually either of the first or of the second order, the chain-carrying reactions are usually of the second order, and the chain-stopping reactions are of the third order or, possibly, of the second order. Since multiple collisions become less likely at reduced pressures we expect chain reactions to be relatively more important at reduced than at elevated pressures. Furthermore, since the diffusion coefficients increase as the pressure is reduced, it is apparent that diffusion transport of active particles must play an increasingly important role in initiating and sustaining chemical reactions, whereas energy transport by thermal conduction must become relatively less important at reduced pressures. As was stated earlier in this discussion, the effect of pressure on adiabatic flame temperature and equilibrium composition is relatively unimportant, although the equilibrium composition of products of dissociation must increase, and the adiabatic flame temperature must decrease, as the pressure is lowered. Nevertheless, it is reasonable to postulate that, as long as the physical dimensions of the chamber are large compared to the dimensions of the reaction zone and the flame remains stable, a decrease in pressure will not alter the qualitative character of the chemical reactions. In particular, one might expect that under these conditions spectroscopic studies of low-pressure flames will provide useful information on the mechanism of combustion. This conclusion is of considerable importance in view of extensive spectroscopic studies of low-pressure flames.

It is useful to regard Eqs. (22) to (24) as phenomenological relations and to inquire how well they correlate available empirical data. For this purpose Eq. (24) may be written in the form

$$\alpha = 2\left[1 + (\partial \ln v/\partial p)\right] \qquad \ldots . \quad (24a)$$

III. QUALITATIVE INFORMATION DERIVABLE FROM FLAME SPECTRA*

The flame spectra obtained in absorption or in emission experiments can be utilized to obtain very precise estimates of the positions of the centers of the spectral lines. A review article by HORNBECK and HERMAN[27] contains a useful compilation of hydrocarbon flame spectra. By the use of well known procedures, which are described in standard texts on spectroscopy[28], the information relating to the positions of the line centers may be utilized to identify the chemical species responsible for the absorption or emission spectrum. For monatomic or diatomic emitters the identification can be carried out unambiguously. For polyatomic molecules the infra-red vibration-rotation bands also permit useful identifications. On the other

* For an excellent survey of flame spectra reference should be made to *Spectroscopy and Combustion Theory* by A. G. GAYDON, Chapman and Hall, London, 1948.

hand, the electronic spectra of polyatomic emitters or absorbers in flames usually cannot be classified unambiguously. The difficulties inherent in the analysis of visible or ultraviolet spectra produced by polyatomic molecules are well exemplified by the controversial history concerning the interpretation of a series of bands frequently observed in flames in the spectral region between 3000 Å and 3700 Å, *viz.*, the hydrocarbon flame bands. These bands have been attributed at various times to HCO[29-31], to superposition of lines belonging to diatomic molecules[32, 33], and to H_2CO*.

The experimental conditions required for observation of emission spectra of atoms, molecules and free radicals are known to spectroscopists and are listed in a book by PEARSE and GAYDON[34], as well as in studies on combustion spectroscopy[27, 30, 35]. It is perhaps noteworthy that some of the chemical species considered to be important for propagating flame reactions (*e.g.* HO_2) are notably unobservable either in emission or in absorption spectra.

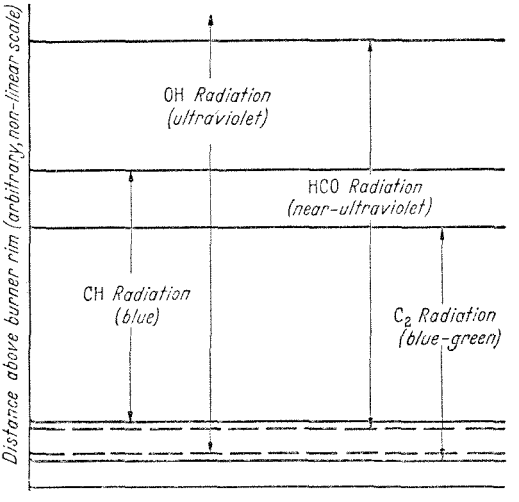


Fig. 1. Radiation characteristics of a low-pressure acetylene-oxygen flame (schematic).

At this point it may be instructive to show schematically a cross section through a representative flame, that indicates the regions in which radiation emitted from different chemical species appears prominently. A two-dimensional flame observed during burning at reduced pressure of a nearly stoichiometric mixture of acetylene and oxygen is shown in *Fig. 1*†. It should be noted that under the indicated conditions the visible thickness of the reaction zone is in the neighborhood of 10 cm. The boundaries between the variously colored regions are very diffuse, presumably as the result of increased diffusion transport without deactivating collision at reduced pressure. The blue-green radiation coming from the portion of the flame closest to the metal duct and above the dark zone is reminiscent of the

* Tentative suggestion advanced by G. A. HORNBECK and R. C. HERMAN, and announced by W. S. BENEDICT at a meeting of the American Physical Society, Pasadena, 1952.

† Results of the type shown in *Fig. 1* have been obtained by GAYDON and WOLFHARD[36], and also by GILBERT in an improved low-pressure burner[37].

light observed in the inner cone of Bunsen flames and is attributed to the presence of C_2. The violet region at the top indicates a marked persistence of CH which radiates in the region between 3900 and 4315 Å. The CH also contributes significantly to the radiation coming from the central blue-white to pink region of the flame. The OH radical begins to radiate at the base of the flame and emits intensely in the ultraviolet region with the hydrocarbon flame bands (presumably due to HCO) furnishing the bulk of near-ultraviolet radiation. Since the hydrocarbon flame bands correspond to a terminal state of oxidation of hydrocarbons, it is not surprising to find them predominating above the strongly luminous reaction zone where the combustion processes have been partly completed and the short-lived intermediates C_2 and CH have been largely oxidized, although HCO begins to radiate even before the CH. The contours of the luminous flame zone vary with mixture ratio and composition. The functional dependence can be determined without difficulty in a qualitative manner. For example, one finds that the intensity of the C_2 radiation decreases as the fuel to oxygen ratio is decreased, and conversely.

IV. QUANTITATIVE INFORMATION DERIVABLE FROM FLAME SPECTRA

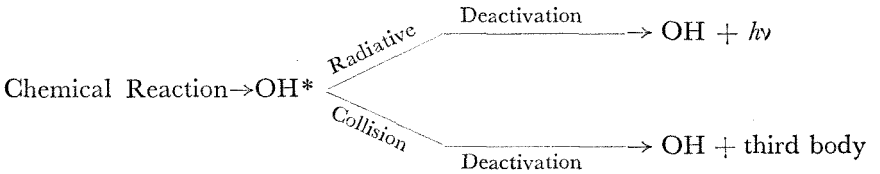
In principle, flame spectra can be used to obtain both concentration and population temperature estimates of the chemical species present in flames. As noted in Section II, the experimental difficulties inherent in the determination of concentrations are such that few if any significant results have been obtained.

A. Experimental evidence for anomalous rotational temperatures in flames— Rotational temperatures have been measured for OH[38-41], CH[42], and C_2[43], in a variety of hydrocarbon flames at atmospheric pressure as well as at reduced pressure. Interesting results have been obtained also in the infra-red region on pre-mixed flames of hydrogen and chlorine[44] and hydrogen and bromine[45]. Finally, results have been obtained recently on diffusion flames[46]. It is not our purpose to present a collection of empirical facts, however valuable they may be. Instead we shall content ourselves with a survey of some of the experimental results described for OH, emphasizing in Section IV*B* the difficulties involved in obtaining an unequivocal interpretation of experimental data.

An exhaustive compilation of the basic spectroscopic data required for measuring rotational temperatures of OH has been prepared by DIEKE and CROSSWHITE[39]. These authors call attention to the possibility of obtaining erroneous values for the rotational temperature if absolute intensities of spectral lines, rather than intensities above the continuous background of the flame, are used. However, it appears that in the experimental studies on low-pressure combustion flames corrections for continuous background are generally unimportant. Thus the experimental findings of GAYDON and WOLFHARD[38], who applied Eq. (6) to all of the clearly resolved rotational lines for $^2\Sigma \rightarrow {}^2\Pi$ transitions of the $v = 0 \rightarrow v = 0$ band of OH, have been considered to be evidence for an abnormal rotational energy distribution of OH in low-pressure combustion flames. It was noted that the apparent rotational temperature of the upper rotational states of OH

in the luminous zone of acetylene–oxygen flames decreased from 8750°K at a pressure of 1·5 mm to 5700°K at 13 mm, remaining almost constant at this value as the pressure was raised to 1 atm. Thus, there appears to be experimental evidence for a more normal rotational distribution of the upper electronic ($^2\Sigma$) state of OH as the pressure is increased. The lower electronic ($^2\Pi$) state of OH seems to exhibit a normal rotational distribution, as suggested by absorption measurements on flames burning at atmospheric pressure[47]. In general, GAYDON and WOLFHARD[38] found that the abnormal rotational excitation of OH was more excessive in rich than in lean mixtures and, for example, much more marked in hydrogen–oxygen flames containing a trace of acetylene than in hydrogen–oxygen flames without acetylene. In order to explain the complicated dependence of T_{rot}" on composition, pressure and position in the flame, Gaydon and Wolfhard started from the premise that during combustion the OH was formed with a thermal rotational population distribution corresponding to a rotational temperature of about 9000°K, *i.e.*, the observed large rotational temperatures were explained in terms of production of OH by chemiluminescent processes. Results similar to those described above have been obtained also by other investigators both at reduced pressures[40] and at atmospheric pressure[41].

An interesting hypothesis to explain the abnormal rotational temperatures of OH has been proposed by GAYDON and WOLFHARD[38]. Briefly their argument is as follows. The emission of radiation from regions of active combustion is the result of deactivation of an excited energy state by the loss of a photon of appropriate energy $h\nu$. Radiative deactivation is always in competition with deactivation by collision. Thus we may represent the processes involved by the following reaction scheme:



Here the star on OH identifies an excited state (*viz.*, the $^2\Sigma$ electronic state in the present case). It is evident that radiative deactivation will be favored by few deactivating collisions and short radiative life of the excited molecule, whereas deactivation by collision will be favored by long radiative life and frequent deactivating collisions. The radiative life of OH in the $^2\Sigma$ state is probably of the order of 4×10^{-6} sec[12, 38]. At a pressure of about 5 mm mercury the time between collisions is in the neighborhood of 10^{-6} sec. As the pressure is raised, the number of collisions during the radiative life of OH* is increased. Hence it is to be expected that the adjustment of the rotational degrees of freedom toward equilibrium should be more complete as the pressure is raised, the effect being very noticeable in the pressure range around a few millimetres since the radiative life and the time between collisions happen to be of the same order of magnitude under these conditions. If the radiative life of OH were much less than 10^{-6} sec, say 10^{-10} sec, then an increase in pressure

from 5 to 500 mm would not have been expected to affect the rotational distribution significantly*.

Nothing has been said in the preceding discussion about reasons for the formation of OH in abnormal rotational energy states. In this connection it may be in order to quote recent theoretical studies by GOLDEN and PEISER[48] on the reaction between hydrogen and bromine at 500°K. These investigators found that the hydrogen bromide first formed exhibited a normal rotational energy distribution not at the temperature of reaction at 500°K but rather at 253°K. Thus, in a relatively simple case, the reaction normally leads to an unexpected rotational distribution. It is not a wide extrapolation from this observation to a suggestion by B. L. CRAWFORD Jr that 'anomalies' in reaction kinetics of the type studied by Golden and Peiser are related to the observed anomalous rotational temperatures in flames.

We have reviewed at some length the experimental evidence for abnormal rotational excitation in OH. The effective rotational excitation in CH has been found to be more nearly normal for most bands although excessive rotational excitation has been observed as well[42]. The rotational temperature of C_2 in regions of active combustion is generally considerably above the adiabatic flame temperature and increases with increasing pressure[43]. Gaydon and Wolfhard favor the view that CH and C_2 are formed with normal rotational energy and are subsequently excited by collision with energy-rich molecules.

B. Distortion of experimental data and apparent rotational temperatures of OH—It is well known[39] that the quantitative interpretation of emission and absorption spectra of OH requires careful corrections for distortion effects which operate in such a way as to produce 'anomalous' rotational temperatures of the type actually recorded for flames. Extensive theoretical studies by the author have been published recently[49, 50] which demonstrate the combined distortions produced by temperature gradients, lack of instrumental resolving power and its relation to spectral line-shape, and by self-absorption (*i.e.*, the concentrations of emitter and absorber are so large that the intensities in emission or absorption are no longer linear functions of the number density and relative integrated intensities needed, for example, in Eq. (6) are no longer measured directly). We shall not reproduce here all of the quantitative arguments which can be raised against the interpretation of the flame spectra of OH reviewed in Section IV*A*. Instead we present in *Table 1* a summary of the arguments which have been put forward, both for and against the reality of anomalous rotational temperatures of OH.

The data listed in *Table 1* are, for the most part, self-explanatory. On the basis of the available experimental evidence, as amplified by extensive theoretical calculations[49, 50], it appears likely that a good many of the reported 'anomalous' rotational temperatures are produced by optical distortion effects. On the other hand, the experimental data, which indicate specific chemical effects, clearly show the persistence of non-equilibrium

* The dependence of apparent rotational temperature on pressure can also be explained satisfactorily by allowing for the expected change of spectral line-shape with pressure (compare Section IV *B*).

distributions in flames and suggest that some of the 'anomalous' rotational temperatures may, in fact, be oversimplified interpretations of non-equilibrium population distributions.

In order to emphasize the care required in interpretation of even the most convincing evidence for abnormal rotational temperatures in flames, we shall now consider more fully the interpretation of the data listed under item (*7*) in *Table 1*.

Gaydon and Wolfhard have found important specific chemical effects on measured intensities and apparent rotational distributions of OH. For example, the radiation from the reaction zone of a pre-mixed hydrogen–oxygen flame shows rotational temperatures not exceeding the adiabatic flame temperature. Introduction of a small amount of acetylene into the reactant gases produces a very large increase in the total intensity and a population distribution in rotational energy levels corresponding to a 'temperature' of about 8000°K for the higher rotational levels. The explanation for this phenomenon advanced by Gaydon and Wolfhard involves the assumption that the observed radiation corresponds to a non-equilibrium mixture of OH at 3000° and at 8000°K with possible production of excited OH (OH*) according to the process

$$CH + O_2 \rightarrow OH^* + CO$$

It may be of interest to examine the experimental data in a somewhat different way by asking if it is not possible to account for the observed results without the introduction of non-equilibrium rotational distributions of OH. As a starting point for this discussion we note experimental studies by Dixon–Lewis[52] as well as theoretical investigations by Hirschfelder and his collaborators[53], which may be summarized by the statement that an enormous concentration of free radicals and atoms is produced in the vicinity of the hot boundary for most chain-reacting flame systems. The concentrations of chain carriers produced have been reported to be many orders of magnitude greater than the thermodynamic equilibrium values. Since the equilibrium concentration of OH in the $^2\Sigma$ state is very small, it is possible that for some flame reactions an enormous increase occurs also in the concentration of OH($^2\Sigma$). It is clear that the occurrence of this phenomenon can easily account for the observed 'abnormal' intensities in emission but it is perhaps less evident that a high concentration of OH($^2\Sigma$), with a population distribution corresponding to 3000°K, can radiate like an 8000°K system provided the concentration of OH in the ground ($^2\Pi$) state corresponds roughly to the thermodynamic equilibrium value. The proof of this last statement is sketched in the last paragraph. To summarize, it appears that the observational data on mixtures of hydrogen, oxygen and acetylene are consistent with:

(*a*) chemiluminescent production of OH and a rotational population distribution at an anomalously high temperature, as suggested by Gaydon and Wolfhard,

(*b*) accumulation in the reaction zone of a high concentration of OH($^2\Sigma$) with a normal rotational distribution, the OH($^2\Sigma$) being possibly produced by a reaction of the type considered by Gaydon and Wolfhard.

In so far as interpretation of flame spectra is concerned it is clear that valuable information regarding the reaction mechanism is obtained if either of the explanations (*a*) or (*b*) is applicable. However, the physical conclusions are quite different. Thus, for case (*a*) we are led to information concerning persistence of abnormal rotation of $OH(^2\Sigma)$ and chemiluminescent production of $OH(^2\Sigma)$, whereas for case (*b*) we obtain information concerning increases in concentration of $OH(^2\Sigma)$, without anomalous rotation, as the result of the chemical reactions propagating the flame. It should be noted, however, that the explanation (*b*) requires not only a large increase of $OH(^2\Sigma)$ but also the production of sufficient $OH(^2\Pi)$ to produce distortion of experimental data through self-absorption. Hence a decision between the interpretations (*a*) and (*b*) is possible by performing

Table 1. Summary of arguments for and against the reality of anomalous rotational temperatures of OH

Arguments for anomalous rotational temperatures	*Arguments against anomalous rotational temperatures*
(*1*) Theoretical calculations on the reaction between H and Br_2 suggest that the HBr first formed has a rotational distribution characteristic of an 'anomalous' temperature[48]	(*1*) In spite of the calculations presented for newly formed HBr one would hardly expect 'anomalous' population distributions, obeying the Maxwell–Boltzmann distribution law, for OH in flames. The production of chemical species under non-equilibrium conditions would not normally be expected to simulate a Boltzmann distribution. For example, the non-equilibrium production of excited electronic states of metal atoms in flames shows a commendably non-Boltzmann character[8].
	(*2*) Interpretation of flame spectra is severely complicated by temperature gradients both along and normal to the line of sight. The distortion of experimental results produced by the combined effects of temperature gradients and self-absorption has not been taken into account in the interpretation of flame spectra. Calculations on non-isothermal systems, using admittedly oversimplified models, suggest that the coupled effects of temperature distortion and self-absorption can be large even under experimental conditions in which the optical density of the emitters and absorbers is surprisingly low[49, 50].
(*3*) Attempts to correct for self-absorption have been made by the use of the iso-intensity method of Dieke and Crosswhite[39]. Direct absorption experiments on flames show very low optical densities for OH thus suggesting that self-absorption does not produce serious distortions[47].	(*3*) As is clear from the work of Dieke and his collaborators, the iso-intensity methods do not correct for self-absorption in isothermal systems if self-absorption is large. The iso-intensity methods are not suitable for correcting the combined distortions produced by temperature gradients and self-absorption. Most of the published absorption experiments have been carried out with continuous radiators as light source. However, absorption for continuous radiation bears a close relation to self-absorption only if the experimental slit width is small compared to the line width. This condition has not been met in the experiments which have been cited as supporting the reality of anomalous rotational temperatures of OH in flames.

Table 1. (Continued)

Arguments for anomalous rotational temperatures	*Arguments against anomalous rotational temperatures*
(*4*) The probable extent of self-absorption in the 'inner cone' of flames may be no larger than in the 'outer cone'. Therefore, if anomalous temperatures are 'observed' in the 'inner cone' they must be real because the 'outer cone' generally yields normal temperatures.	(*4*) On the basis of the best available absolute intensity data for OH[12], and by using equilibrium estimates for concentrations of OH, it appears that self-absorption distortions should be expected in many representative flames[51]. Since the chemical reactions in the reaction zone are not understood in any detail it is not proper to assume that the concentration of OH in regions of active combustion will not be larger than the equilibrium concentration. Hence it is not justifiable to postulate that distortion by self-absorption is not more important for the 'inner cone' than for the 'outer cone'. Similarly, distortion by temperature gradients would be expected to be entirely different for the 'inner' and 'outer' cones.
(*5*) Absorption experiments on flames invariably yield 'normal' temperatures thus showing a normal rotational distribution for the $^2\Pi$ state. For the same flames the $^2\Sigma$ state yields abnormal rotational temperatures. Hence the anomalous temperatures for the $^2\Sigma$ state must be real.	(*5*) Quantitative calculations for spectral lines with Doppler contour under isothermal conditions predict precisely the observed result[49]. Thus, fortuitously, distortion by self-absorption in absorption experiments turns out to be much weaker than in emission experiments for the same numerical value of the self-absorption parameters.
(*6*) As the pressure is reduced the 'anomalous' flame temperatures of OH become still more 'anomalous'[38]. Since one might expect a decrease in the optical density of OH with decreasing pressure, this result shows that we are dealing with a truly chemiluminescent radiation.	(*6*) Although the absolute value for the partial pressure of OH is decreased as the pressure is reduced, the decrease in optical density does not really occur in representative low-pressure flames. On the other hand, as the pressure is reduced the line-shape must change from combined Doppler and collision broadening to nearly pure Doppler broadening. However, it has been shown that this expected change of line-shape, for isothermal systems, must lead to a large increase in apparent rotational temperature as the pressure is reduced[50]. Thus the observed variation of rotational temperature with pressure actually constitutes a strong argument against the reality of the anomalous temperature.
(*7*) In several flames specific effects have been observed which cannot be reconciled with equilibrium theory. For example, the 'inner cone' of a hydrogen-oxygen flame exhibits 'normal' temperatures until a small amount of acetylene is introduced into the flame. The 'anomalous' rotational temperature associated with the introduction of acetylene proves the reality of the phenomenon[38].	(*7*) There appears to be no question about the fact that introduction of acetylene into a pre-mixed flame of hydrogen and oxygen produces a pronounced change in the nature of the combustion reactions. However, it is not at all certain that the observed 'non-equilibrium phenomenon' indicates an anomalous rotational temperature. It may also indicate the production of large concentrations of OH in the excited electronic ($^2\Sigma$) state in the inner cone (compare the discussion given in the text).

difficult quantitative absorption experiments to estimate concentrations for $OH(^2\Pi)$, which must be greater in the reaction zone for hydrogen–oxygen flames containing acetylene than for flames not containing acetylene if explanation (*b*) is to be acceptable. Depending on the length of the radiating path, the concentration of $OH(^2\Pi)$ required may be less than, about equal to, or greater than the theoretical equilibrium values, whereas the concentration of $OH(^2\Sigma)$ must increase sufficiently to account for the observed total change in emitted intensity.

The fact that an isothermal non-equilibrium mixture of $OH(^2\Sigma)$ and $OH(^2\Pi)$ at 3000°K can radiate like a mixture of OH at 3000°K and at 8000°K follows immediately if the appropriate transfer equations are formulated as originally done by K. SCHWARZSCHILD in 1905. For unit area of receiver oriented normal to the emitted radiation, the differential change in a distance dx of the spectral intensity of radiation I_ν is

$$dI_\nu = -P_\nu dx p I_\nu + \varepsilon_\nu p dx \quad \ldots . \quad (26)$$

where P_ν is the spectral absorption coefficient (in cm^{-1} — atm^{-1} of OH), p equals the partial pressure of OH, I_ν is the spectral intensity at the position x, and ε_ν is the spectrally emitted intensity. For an equilibrium ratio of $OH(^2\Sigma)$ to $OH(^2\Pi)$ we would set $\varepsilon_\nu = P_\nu R_\nu$ where R_ν is the spectral intensity of radiation emitted from a black body at 3000°K. For the assumed non-equilibrium ratio of $OH(^2\Sigma)$ to $OH(^2\Pi)$ it is necessary to write $\varepsilon_\nu = \alpha P_\nu R_\nu$ where α is a constant measuring the magnification of the concentration of $OH(^2\Sigma)$. Integrating Eq. (26) from $I_\nu = 0$ at $x = 0$ to $I_\nu = I_\nu'$ at $x = l$ leads to the result

$$I_\nu' = \alpha R_\nu [1 - \exp(-P_\nu p l)] \quad \ldots . \quad (27)$$

It is evident that a repetition of our quantitative studies on self-absorption[49], starting with Eq. (27), will lead to the same results as before except that the ordinate in conventional plots for the interpretation of flame spectra is increased by $\log\alpha$. In other words, an isothermal system at 3000°K containing a non-equilibrium ratio of $OH(^2\Sigma)$ to $OH(^2\Pi)$ will radiate with a hundredfold increase in intensity for $\alpha = 100$ compared to a system with an equilibrium concentration of $OH(^2\Sigma)$ and of $OH(^2\Pi)$. The apparent rotational temperature will be 8000°K in either case for a sufficiently high concentration of $OH(^2\Pi)$.

C. Vibrational temperatures—Vibrational temperature measurements in flames may or may not exhibit abnormal values. SHULER[54] has reported excessive vibrational temperatures of OH in atmospheric flames of acetylene–oxygen. It is possible to account for these anomalous vibrational temperatures in terms of distortion effects similar to those discussed in Section IV*B* for the 'abnormal' rotational temperatures, although the persistence of vibrational non-equilibrium is *a priori* more probable than that of rotational non-equilibrium.

D. Electronic temperatures in low-pressure combustion flames—Extensive line reversal measurements to estimate electronic temperatures of atoms in low-pressure combustion flames have been carried out by GAYDON and WOLFHARD[8]. The results of these measurements, which suggest non-equilibrium electronic excitation, have been considered in Section I*C*.

E. Translational temperatures in low-pressure combustion flames—Perhaps the most startling results which have thus far been obtained in low-pressure flame spectroscopy are translational temperature measurements on CH using the Doppler contour method described in Section I*B*. Thus GAYDON and WOLFHARD[6] report that the observed data on the line-shape of the CH bands followed Eq. (11), thereby indicating a Maxwellian velocity distribution of the molecules. However, the measured translational temperature was 4000°K in a stoichiometric acetylene–oxygen flame at pressures between 2 and 14 mm, whereas the adiabatic flame temperature is known to be less than 3000°K. The apparent values of the translational temperature were found to increase regularly from the bottom of the flame through the reaction zone to the top of the flame. At atmospheric pressure the observed translational temperature was found to be normal, still assuming a Doppler contour for the spectral line-shape.

The experimental difficulties involved in the determination of translational temperatures by the use of line contour studies are considerable, as is evident by reference to the work of Gaydon and Wolfhard. Nevertheless, it is not easy to invent reasonable optical distortion effects of sufficient magnitude to explain quantitatively the experimental data without the use of surprisingly short rotational life times and anomalous 'translational temperatures' for CH. The Doppler half-width method for measuring the translational temperatures of individual chemical species deserves more extensive application to combustion spectroscopy than it has received thus far.

V. COMBUSTION KINETICS, FLAME PROPAGATION AND COMBUSTION SPECTROSCOPY

The more widely quoted theories on the mechanism of hydrocarbon combustion are discussed in the well known book by LEWIS and VON ELBE[55]. Free radicals such as C_2 and CH, which play a prominent role in combustion spectroscopy, do not occur as essential intermediates in any of the principal reaction schemes. They may be formed as the result of side reactions which do not influence the principal course of the combustion process. Perhaps they are so prominent in flames because the radiative life of the excited state is short compared to the time required for deactivation by collision. A representative reaction, which has been proposed for the formation of excited CH and is sufficiently exothermic to produce the excited free radical[56], is the following:

$$C_2 + OH \rightarrow CH^* + CO$$

The mechanism of formation of C_2 is not well understood; C_2 appears equally strongly in flames of acetylene and in flames of higher hydrocarbons ; it is therefore probably not the result of thermal cracking.

The results of combustion spectroscopy have not yet had a profound influence on the formulation of the probable rate-controlling kinetic processes occurring in flames. The relation between spectroscopic studies on flames and detailed reaction steps occurring in flames has been considered particularly by LAIDLER and his collaborators[57]. The ultimate use of

results obtained by combustion spectroscopists for predicting velocities of flame propagation through a molecular theory appears very remote.

It appears appropriate to note that a really concerted attack upon a simple combustion problem, *e.g.* a study of the ozone or hydrazine decomposition flames, may be a more fruitful endeavor at the present time than the more ambitious programs involving hydrocarbon combustion which have been pursued in the past. If we were certain that all that is required to predict the gross behavior of flames, *i.e.* the velocity of normal flame propagation, is a detailed knowledge of every conceivable reaction step, we might be inclined to regard the problem of flame propagation as solved in principle but almost hopelessly complex in detail. Presumably the non-equilibrium theories of reaction rates developed by PRIGOGINE[58] and CURTISS[59] have already established this conclusion. Nevertheless, it is evidently desirable to show, for example, that the detailed reaction mechanism of the hydrogen–bromine flame, coupled with detailed spectroscopic studies of population temperatures and concentration estimates, is consistent with GOLDEN's kinetics of reactions[48] and with the detailed theory of one-dimensional flame propagation.

In conclusion we shall restate briefly what appears to be the significant relation between spectroscopic studies on flames and determination of eigenvalues for the mass flow rate in laminar flame propagation. Spectroscopic studies of regions of active combustion are necessarily limited to a selected group of compounds which happen to possess spectroscopic transition probabilities and spectral lines that make them suitable for experimental study with conventional instrumentation. It is commonly acknowledged by combustion spectroscopists that the chemical species on which observations are made may not play a vital role in the rate-controlling chemical reactions occurring during combustion. Nevertheless, it is possible that ultimately detailed spectroscopic studies of flames will not only give an insight into the nature of specific chemical reactions, which can be studied, but will also provide an answer to the very basic question concerning the use of reaction rates determined under isothermal conditions for the study of rate processes in flames, shock fronts *etc.*

FRENCH SUMMARY

On présente une revue critique des résultats obtenus par observation spectrographique des flammes. Le but de cette étude est d'examiner l'état actuel, les possibilités et les limitations de la spectrographie appliquée aux problèmes de combustion en vue (a) *d'éclaircir le mécanisme de la combustion et* (b) *de résoudre des problèmes techniques de combustion. Comme d'importantes études ont été effectuées sur les flammes à basse pression on donne également une discussion de l'effet probable de la pression sur la célérité des flammes laminaires.*

REFERENCES

[1] CHAPMAN, S. and COWLING, T. G. *The Mathematical Theory of Non-Uniform Gases* pp. 237–241 ; Cambridge University Press, Cambridge, 1939

[2] MAYER, J. E. and MAYER, M. G. *Statistical Mechanics* pp. 83–85 ; John Wiley, New York, 1940

[3] SHULER, K. E. " Kinetics of OH Radicals from Flame Emission Spectra. II " *J. chem. Phys.* Vol. 18, pp. 1466–1470, 1950

[4] MARGENAU, H. and WATSON, W. W. " Pressure Effects on Spectral Lines " *Rev. Mod. Phys.* Vol. 8, pp. 22–53, 1936

VAN VLECK, J. H. and WEISSKOPF, V. F. " On the Shape of Collision-Broadened Lines " *ibid* Vol. 17, pp. 227–236, 1945

ANDERSON, P. W. " Pressure Broadening in the Micro-wave and Infra-Red Regions " *Phys. Rev.* Vol. 76, pp. 647–661, 1949

[5] JENKINS, F. A. and WHITE, H. E. *Fundamentals of Physical Optics* Chapter 4 ; McGraw-Hill, New York, 1937

[6] GAYDON, A. G. and WOLFHARD, H. G. " Spectroscopic Studies of Low-Pressure Flames. II. Effective Translational and Rotational Temperatures from CH Bands " *Proc. roy. Soc. A* Vol. 199, pp. 89–104, 1949

[7] VAN DER HELD, E. M. F. " Intensity and Natural Breadth of Spectral Lines " *Z. Phys.* Vol. 70, pp. 508–515, 1931

UNSOLD, A. *Physik der Sternatmosphären* pp. 159–169 ; J. W. Edwards, Ann Arbor, Michigan, 1948

PENNER, S. S. and KAVANAGH, R. W. " Radiation from Isolated Spectral Lines with Combined Doppler and Lorentz Broadening " *J. opt. Soc. Amer.* Vol. 43, pp. 385–388, 1953

[8] GAYDON, A. G. and WOLFHARD, H. G. " Spectroscopic Studies of Low-Pressure Flames. V. Evidence for Abnormally High Electronic Excitation " *Proc. roy. Soc. A* Vol. 205, pp. 118–134, 1951

[9] BAUER, E. " Radiation and Temperature of Flames " *Radium, Paris* Vol. 6, pp. 110–117, 1909

[10] HENNING, F. and TINGWALDT, C. " The Temperature of the Acetylene–Oxygen Flame " *Z. Phys.* Vol. 48, pp. 805–823, 1928

[11] KING, R. B. and STOCKBARGER, D. C. " Absolute f-Values by the Method of Total Absorption " *Astrophys. J.* Vol. 91, pp. 488–502, 1940

— " Absolute f-Values for Lines of Fe I ; Abundance of Iron in the Sun " *ibid* Vol. 95, pp. 78–81, 1942

BIERMANN, L. and LÜBECK, K. " Transition Probabilities of a Number of Spectral Lines of Different Atoms and Ions and Normalized Wave Functions of the Requisite Atomic States " *Z. Astrophysik.* Vol. 25, pp. 325–329, 1948

[12] OLDENBERG, O. and RIEKE, F. F. " Kinetics of OH Radicals as Determined by Their Absorption Spectrum. III. A Quantitative Test for Free OH ; Probabilities of Transition " *J. chem. Phys.* Vol. 6, pp. 439–447, 1938

DWYER, R. J. and OLDENBERG, O. " The Dissociation of H_2O into H + OH* " *ibid* Vol. 12, pp. 351–361, 1944

[13] SHULL, H. " Transition Probabilities. III. Dipole Velocity Computations for C_2 and N^{2+}. The Degree of Hybridization " *ibid* Vol. 20, pp. 1095–1102, 1952 (see also earlier papers by the same author, referred to in this publication)

[14] MULLIKEN, R. S. " Intensities of Electronic Transitions in Molecular Spectra " *ibid* Vol. 7, pp. 14–20, pp. 20–34, pp. 121–135, pp. 339–352, pp. 353–356 *etc,* 1939

[15] WILSON, E. B. Jr and WELLS, A. J. " The Experimental Determination of the Intensities of Infra-Red Absorption Bands. I. Theory of the Method " *ibid* Vol. 14, pp. 578–580, 1946

THORNDIKE, A. M., WELLS, A. J. and WILSON, E. B. Jr. " The Experimental Determination of the Intensities of Infra-Red Absorption Bands. II. Measurements on Ethylene and Nitric Oxide " *ibid* Vol. 15, pp. 157–165, 1947

[16] THORNDIKE, A. M., " The Experimental Determination of Infra-Red Intensities, III. Carbon Dioxide, Methane, and Ethane " *J. chem. Phys.* Vol. 15, pp. 868–874, 1947

[17] PENNER, S. S. and WEBER, D. " Quantitative Infra-Red Intensity Measurements " *ibid* Vol. 19, pp. 807–816, pp. 817–818, and pp. 974–975, 1951 ; Vol. 21, pp. 649–654, 1953

[18] FRANCIS, S. A. " Absolute Intensities of Characteristic Infra-Red Absorption Bands of Aliphatic Hydrocarbons " *ibid* Vol. 18, pp. 861–865, 1950

[19] CALLOMON, H. J., MCKEAN, D. C. and THOMPSON, W. H. " Intensities of Vibration Bands. IV. Carbonyl Sulphide and Acetylene " *Proc. roy. Soc. A* Vol. 208, pp. 341–351, 1951 (see also earlier papers by Thompson and collaborators, referred to in this article)

[20] PENNER, S. S. " A Two-Path Method for Measuring Flame Temperatures and Concentrations in Low-Pressure Combustion Chambers " *J. chem. Phys.* Vol. 19, pp. 272–280, 1951

[21] — " A Two-Path Method for Eliminating the Effects of Self-Absorption on Temperature for Isothermal Flames " *ibid* Vol. 20, pp. 1341–1342, 1952

[22] HIRSCHFELDER, J. O. and CURTISS, C. F. " The Theory of Flame Propagation " *ibid* Vol. 17, pp. 1076–1081, 1949

— — " The Theory of Flame Propagation. II " *J. phys. Chem.* Vol. 55, pp. 774–788, 1951

[23] — BIRD, R. B. and SPOTZ, E. L. " The Transport Properties for Non-Polar Gases " *J. chem. Phys.* Vol. 16, pp. 968–981, 1948

[24] WOLFHARD, H. G. " Properties of Stationary Flames at Reduced Pressure " *Z. tech. Phys.* Vol. 24, pp. 206–211, 1943

[25] TANFORD, C. and PEASE, R. N. " Equilibrium Atom and Free Radical Concentrations in Carbon Monoxide Flames and Correlation with Burning Velocities " *J. chem. Phys.* Vol. 15, pp. 431–433, 1947

— " Theory of Burning Velocity. I. Temperature and Free Radical Concentrations Near the Flame Front, Relative Importance of Heat Conduction and Diffusion " *ibid* Vol. 15, pp. 433–439, 1947

— and PEASE, R. N. " Theory of Burning Velocity. II. The Square Root Law for Burning Velocity " *ibid* Vol. 15, pp. 861–865, 1947

[26] STEACIE, E. W. R. *Atomic and Free Radical Reactions* Reinhold Publishing Corporation, New York, 1946

[27] HORNBECK, G. A. and HERMAN, R. C. " Hydrocarbon Flame Spectra " *Industr. Engng Chem.* Vol. 43, pp. 2739–2757, 1951

[28] HERZBERG, G. *Atomic Spectra and Atomic Structure* Dover Publications, New York, 1944

— *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* D. Van Nostrand, New York, 1950

— *Molecular Spectra and Molecular Structure. II. Infra-Red and Raman Spectra of Polyatomic Molecules* D. Van Nostrand, New York, 1951

[29] VAIDYA, W. M. " Isotope Effect in Hydrocarbon Flame Bands " *Proc. phys. Soc. Lond. A* Vol. 64, pp. 428–430, 1951

[30] GAYDON, A. G. *Spectroscopy and Combustion Theory* Chapman and Hall, London, 1948

[31] DYNE, P. J. and STYLE, D. W. G. " Radical Spectra in Fluorescence " *Disc. Faraday Soc.* No. 2, pp. 159–161, 1947

[32] HERMAN, R. C. and HORNBECK, G. A. " Hydrocarbon Flame Spectra " *J. chem. Phys.* Vol. 17, p. 1344, 1949

[33] HORNBECK, G. A. and HERMAN, R. C. " Further Studies of Hydrocarbon Flame Spectra " *ibid* Vol. 18, pp. 763–764, 1949

[34] PEARSE, R. W. B. and GAYDON, A. G. *The Identification of Molecular Spectra* John Wiley, New York, 1950

[35] GAYDON, A. G. " The Emission Spectra of Flames " *Quart. Rev. chem. Soc. Lond.* Vol. 4, pp. 1–19, 1950

[36] — and WOLFHARD, H. G. " Free Radicals in Low-Pressure Flames " *Disc. Faraday Soc.* No. 2, pp. 161–166, 1947

[37] GILBERT, M. " The Investigation of Low-Pressure Flames " *Report No. 4–54*, Jet Propulsion Laboratory, Pasadena, August 1949

[38] GAYDON, A. G. and WOLFHARD, H. G. " Spectroscopic Studies of Low-Pressure Flames " *Proc. roy. Soc. A* Vol. 194, pp. 169–184, 1948

[39] DIEKE, G. H. and CROSSWHITE, H. M. " The Ultraviolet Bands of OH " *Bumblebee Series Report No. 87*, The Johns Hopkins University, Baltimore, Maryland, November 1948

[40] PENNER, S. S., GILBERT, M. and WEBER, D. " Spectroscopic Studies of Low-Pressure Combustion Flames " *J. chem. Phys.* Vol. 20, pp. 522–523, 1952

[41] BROIDA, H. P. and LALOS, G. T. " Rotational Temperatures of OH in Several Flames " *ibid* Vol. 20, pp. 1466–1471, 1952

[42] GAYDON, A. G. and WOLFHARD, H. G. " Spectra of Flames Supported by Free Atoms " *Proc. roy. Soc. A* Vol. 213, pp. 366–378, 1952

[43] — — " Spectroscopic Studies of Low-Pressure Flames. III. Effective Rotational Temperatures and Excitation Mechanism for C_2 Bands " *ibid A* Vol. 201, pp. 561–569, 1950

[44] NEWMAN, R. " Emission Spectrum of HCl in the Near Infrared " *J. chem. Phys.* Vol. 20, pp. 749–750, 1952

[45] BULLOCK, B. W., FEAZEL, C. E., GLOERSEN, P. and SILVERMAN, S. " The Flame Emission Spectrum of HBr " *ibid* Vol. 20, pp. 1808–1809, 1952

[46] WOLFHARD, H. G. and PARKER, W. G. "A New Technique for the Spectroscopic Examination of Flames at Normal Pressures" *Proc. phys. Soc. Lond. A* Vol. 62, pp. 722–730, 1949

— — "A Spectroscopic Investigation into the Structure of Diffusion Flames" *ibid A* Vol. 65, pp. 2–19, 1952

[47] BROIDA, H. P. "Rotational Temperatures of OH in Methane–Air Flames" *J. chem. Phys.* Vol. 19, pp. 1383–1390, 1951

[48] GOLDEN, S. and PEISER, A. M. "Quantum Mechanics of Chemical Kinetics of Homogeneous Gas Phase Reactions. II. Approximations for Displacement Reactions Between an Atom and a Diatomic Molecule" *J. chem. Phys.* Vol. 17, pp. 630–643, and p. 842, 1949

[49] PENNER, S. S. "Quantitative Studies of Apparent Rotational Temperatures of OH in Emission and Absorption (Spectral Lines with Doppler Contour)" *ibid* Vol. 21, pp. 31–41, 1953

[50] — "Effect of Spectral Line-Shape on Apparent Rotational Temperatures of OH" *ibid* Vol. 21, pp. 686–688, 1953

[51] — "Emission and Absorption of Radiation by Spectral Lines with Doppler Contour" *ibid* Vol. 20, pp. 507–510, 1952

[52] DIXON-LEWIS, G. Fourth Symposium on Combustion, M.I.T., Cambridge, September 1952

[53] HIRSCHFELDER, J. O., CURTISS, C. F. and CAMPBELL, D. E. "The Theory of Flame Propagation and Detonation, IV" *Report CM 756*, University of Wisconsin Naval Research Laboratory, Madison, November 1952

[54] SHULER, K. E. "Kinetics of OH Radicals from Flame Emission Spectra. I. Vibrational Transition Probabilities, Intensities, and Equilibrium in the $^2\Sigma \rightarrow {}^2\Pi$ Transition" *J. chem. Phys.* Vol. 18, pp. 1221–1226, 1950

[55] LEWIS, B. and VON ELBE, G. *Combustion, Flames and Explosions of Gases* Chapter IV ; Academic Press, New York, 1951

[56] PANNETIER, G. and GAYDON, A. G. "On a Mechanism of Reaction for the Formation of the Free Radicals C_2, CH, and OH" *C.R. Acad. Sci., Paris* Vol. 225, pp. 1300–1302, 1947

[57] HERMAN, R. C., HORNBECK, G. A. and LAIDLER, K. J. "Kinetic Mechanism and Hydrocarbon Flame Spectra" *Science*, Vol. 112, pp. 497–498, 1950

GRIFFING, V. F. and LAIDLER, K. J. "The Mechanism of Some Elementary Reactions Occurring in Flames. I. The Carbon Monoxide Flame" *Third Symposium on Combustion, Flame and Explosion Phenomena* pp. 432–441 ; Williams and Wilkins, Baltimore, 1949

LAIDLER, K. J. and SHULER, K. E. "Kinetics of Combustion in Relation to Emission Flame Spectroscopy" *Industr. Engng Chem.* Vol. 43, pp. 2758–2761, 1951

[58] PRIGOGINE, I. "The Equilibrium Hypothesis in Chemical Kinetics" *J. phys. Chem.* Vol. 55, pp. 765–774, 1951

[59] CURTISS, C. F. *Ph.D. Thesis* University of Wisconsin, Madison, 1950